

Active site separation of photocatalytic steam reforming of methane using Gas-Phase Photoelectrochemical system

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Methods

Synthesis of Pt/YSZ powder catalysts

The Pt-loaded YSZ powder catalyst (Pt/YSZ) used in this study was synthesized by an impregnation method using commercially available YSZ powder ($ZrO_2/5.2\%Y_2O_3$: 3 mol% Y_2O_3 , <3 microns, Stream Chemicals, Inc) as a supporter. We used Pt as a co-catalyst because it has been used for photocatalytic SRM¹⁻³. For the deposition procedure of Pt, the mass ratio of Pt to YSZ was weighed to be 1%, and the beaker containing YSZ and Hydrogen hexachloroplatinate(IV) hexahydrate solution (Kanto Chemical Co., Ltd.) was heated with stirring until the water evaporated. The dried powder was ground in a mortar and a pestle, then placed in a tube furnace with an H_2 flow rate of 60 ml/min. Heating up to 500 °C in 2h and holding it for 2 h resulted in the reduction of Pt precursor to the metallic phase to obtain Pt/YSZ powder.

Cell fabrication

The YSZ pellet was used as a solid electrolyte because of its high oxygen ions conductivity. Highly dispersed powder catalyst pastes were prepared as shown in Figure S3(a) for coating it as catalyst layer (electrode layer) on the commercial YSZ pellet (ZR-8Y disk, 8 mol% Y_2O_3 , 24 mm in diameter, 0.25 mm thick, Nikkato Co.) by screen printing. To prepare highly dispersed powder catalyst paste, two polymers, 1.5 g of ethyl cellulose (Sigma-Aldrich Co., assay: 48.0-49.5% (w/w) ethoxyl basis, form: coarse powder, viscosity: 30-70 mPa.s, 5 % in toluene/ethanol 80:20 (25 °C)) and 3.0 g of ethyl cellulose (Sigma-Aldrich Co., assay: 48.0-49.5% (w/w) ethoxyl basis, form: powder, viscosity: 7-15 mPa.s, 6 % in toluene/ethanol 80: 20 (25 °C)) were added to a lidded bottle containing 45 mL of ethanol, and the solution was stirred at 60 °C using a hot stirrer to obtain an ethanol solution of ethyl cellulose. Next, 1.0 g of the synthesized Pt/YSZ powder catalyst was added to 50 ml of ethanol in a beaker and sonicated for 15 min. 4.075 ml of the obtained ethanol solution of ethyl cellulose was added to this suspension of Pt/YSZ powder catalyst, and the ethanol was evaporated at 95°C with stirring. Before the ethanol completely evaporated, 3.056 ml of α -terpineol (Kanto Chemical Co., Ltd.) was added. After the ethanol was evaporated, the obtained paste was placed in a container and stirred with a rotation/revolution mixer (ARE-310, THINKY Co.) for 60 seconds at 500 rpm, 40 seconds at 2000 rpm, 40 seconds at 1500 rpm, and 60 seconds at 500 rpm. By stirring, the highly dispersed powder catalyst paste for screen printing was obtained. The obtained highly dispersed powder catalyst paste was screen printed on one side of the YSZ pellet as shown in Figure S3(b) and dried at 105°C. Then, the highly dispersed powder catalyst paste was screen printed on the other side and dried at 105°C. After drying, the pellet was sintered in an electric furnace at 900°C (temperature increased in 3h and held for 2h) under an air condition. Then, the pellet was placed in a tube furnace and H_2 was flowed at a flow rate of 60 ml/min at 500°C (temperature increased in 2h and held for 2h) to reduce the Pt particles to obtain the cell used in the GPEC system. The loaded Pt in the Pt/YSZ powder, screen printed on both sides of the pellet, plays an essential role in the GPEC system to guarantee its electronic contact.

Sample characterizations

XRD measurements of the Pt/YSZ powder catalyst, the YSZ pellet, and the cell screen printed with the Pt/YSZ powder catalyst on YSZ pellets were performed using Rigaku SmartLab with a Cu K α X-ray as a X-ray source. The Pt/YSZ powder catalyst was measured by a convergence method (Bragg-Brentano BB), while the YSZ pellet and the cell with the Pt/YSZ powder catalyst screen printed on the YSZ pellet were measured by the thin-film method (parallel beam method, PB) to get the signal of the thin Pt/YSZ catalyst layer on the YSZ pellet. The incident angle of the X-rays was set to 0.4°. The microstructure of the Pt/YSZ powder catalyst was observed by transmission electron microscopy (TEM, JEM-2010F, JEOL *Ltd.*) at an acceleration voltage of 200 kV. The cross-section of the fabricated cell was observed using a scanning electron microscope (SEM, VE-9800SP, KEYENCE Co.) at an acceleration voltage of 15 kV and a WD of 8.9 mm. Before the observation, gold sputtering was performed using a magnetron sputtering system (MSP-mini, VACUUM DEVICE). UV-Vis absorption spectra of the YSZ powder and the Pt/YSZ powder catalyst were measured by diffuse reflection method using a UV-Vis IR spectrophotometer (V-670, JASCO Co.). In the Tauc plot, the vertical axis is $(F(R)hv)^{1/r}$, and the horizontal axis is hv . $F(R)$, h , and v were the Kubelka-Munk value obtained from the absorption spectrum, Planck's constant, and the frequency of light, respectively. In the vertical axis $(F(R)hv)^{1/r}$, $r=1/2$ was used by assuming ZrO₂ as a direct semiconductor. To analyze the photogenerated carriers in the Pt/YSZ powder catalyst during light irradiation, ESR measurements were performed using an operando electron spin resonance system (EMX nano, Bruker BioSpin) which could analyze the excited charge carriers under controlled atmosphere and light irradiation as shown in Figure S4. We introduced the powder catalyst into a quartz tube and performed the ESR measurement at 100K cooled with liquid nitrogen.

Photocatalytic SRM activity of Pt/YSZ powder catalyst

The photocatalytic SRM activities of the Pt/YSZ powder catalyst were evaluated at various temperatures under dark conditions and UV irradiation with a 150 W Hg-Xe lamp (LA-410UV-5, HAYASHI-REPIC CO., LTD.). The spectra of the Hg-Xe lamp were measured in case long pass cutoff filters (HAYASHI-REPIC CO., LTD.) 250 nm, 275 nm, and 300 nm were used.

The SRM on the Pt/YSZ powder catalyst was performed in a flow reactor equipped with a quartz window under ambient pressure as shown in Figure S5. In this flow reactor, light could be irradiated to the powder catalyst through the quartz window. The powder catalyst (15 mg) was placed in a ceramic porous cup, and the cup was set in the flow reactor. A gas mixture of approximately Ar: CH₄ = 99: 1 vol% was conditioned to contain 1 vol% water vapor using a precision humidity regulator (me-39DPRT-MFC-FH-SUS, micro equipment Inc.) and continuously supplied into the flow reactor at a flow rate of 10 mL/min using a mass flow controller. The flow reactor was sufficiently purged with the supplied gas, and then the photocatalytic SRM was performed with various reactor temperatures. The amounts of produced H₂, CO, and CO₂ were measured with a micro GC (MGC3000A, INFICON Co.,Ltd).

The action spectra of the SRM on the Pt/YSZ powder catalyst were obtained using long pass cutoff filters of

250 nm, 275 nm, and 300 nm between the Hg-Xe lamp and the quartz window. The reaction temperature was set at 500°C.

Gas-Phase Photoelectrochemical system (GPEC system)

The GPEC system was used to separate the oxidation and reduction sites of the SRM using the fabricated cell. This GPEC system was developed by Kushida et al. in collaboration with Chino Corporation.⁴ The gas used for the reaction was supplied separately to the anode and cathode side holders after controlling the flow rate with a mass flow controller. Furthermore, the potentiostat allowed us to control electrode potential and enabled electrochemical measurements. The gas passing through the holder reacted on the anode and cathode sides separately and could be analyzed by gas chromatography. The holder part could be placed in an electric furnace to control the temperature during the reaction. The holder part and the electric furnace were equipped with quartz windows to allow light to be irradiated to both the anode and cathode sides of the cell. The distance from the quartz window on the electric furnace to the cell on the holder was approx. 14 cm. This GPEC system was connected to an electrochemical measurement system (HZ-7000, Hokuto Denko Co.). A gas mixture of Ar: CH₄ = 99: 1 vol% was supplied to the anode side at a flow rate of 150 ml/min, and a gas containing water vapor by bubbling Ar gas with a water-filled bubbler at room temperature was supplied to the cathode side at a flow rate of 150 ml/min. The electric furnace was used to control the reaction temperature and set at 700°C to promote sufficient oxygen ions conduction. The UV light was irradiated from both the anode and cathode sides using Hg-Xe lamps (LA-410UV-5, HAYASHI-REPIC CO., LTD.). The gas chromatograph (GC-2010 Plus, Shimadzu Co.) equipped with a barrier discharge ionization detector (BID) using a micropacked column (MICROPACKED ST, Shinwa Chemical Industries Ltd.) was used to analyze the gases produced from the anode and cathode sides separately.

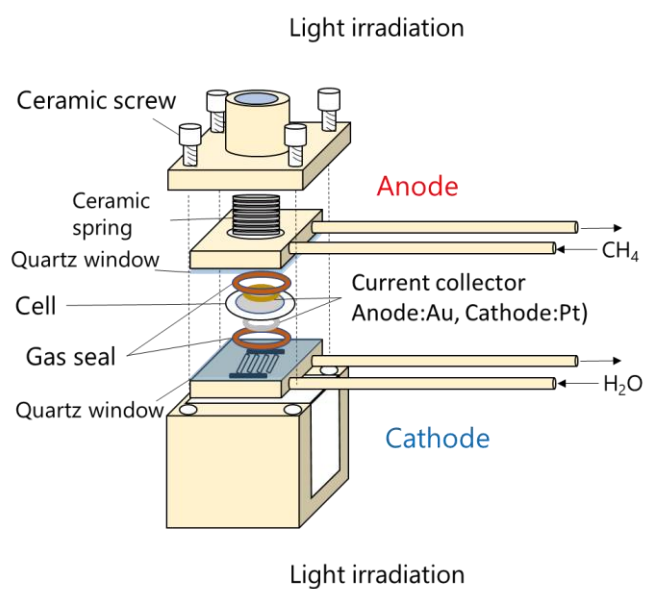
Before performing the light irradiation experiments in the GPEC system, the transmitted light of the cell was measured by a spectroradiometer to investigate the effect of the transmitted light on the opposite side of the cell as shown in Figure S6. The irradiation distance between the Hg-Xe lamp and the spectroradiometer was set to the identical distance between the Hg-Xe lamp and the cell in the GPEC system.

The surface temperature of the cell was measured using a radiation thermometer to investigate the temperature rise of the cell due to light irradiation. The cell was placed in the flow reactor as shown in Figure S7, and the distance between the Hg-Xe lamp and the cell was the identical distance to that in the GPEC system. First, the temperature of the reactor was set to the reaction temperature in the GPEC system (700 °C), and the radiation thermometer (FLHX-TNE0090-0200B003-000, Japan Sensor Co.) was calibrated. Then, UV light was irradiated and the surface temperature of the cell was measured when the temperature of the radiation thermometer got stabilized.

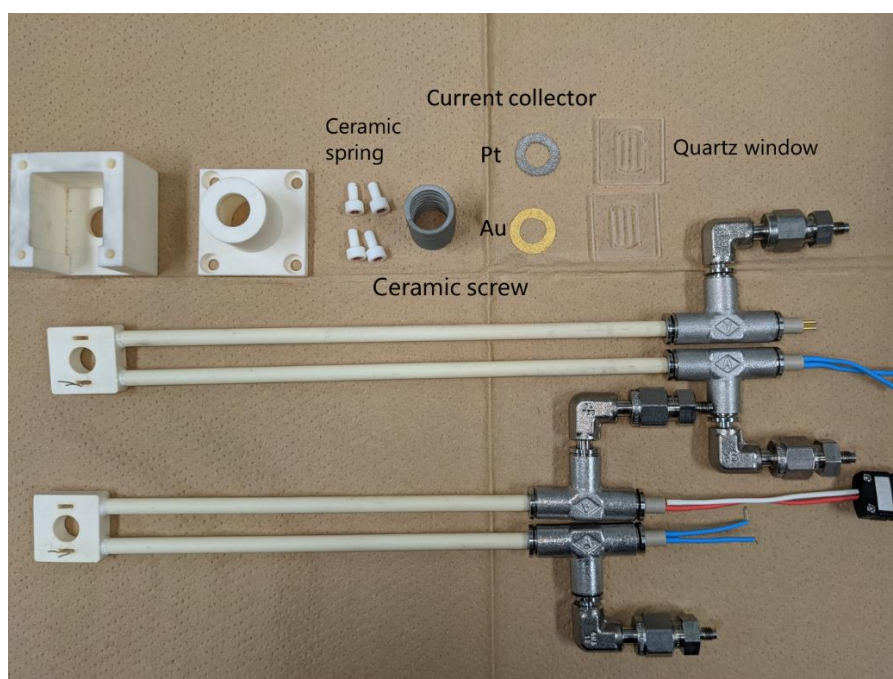
Using the GPEC system, the voltage change was measured by the electrochemical measurement system under constant current (Galvanostat) conditions when UV light (Hg-Xe lamps) was irradiated from both sides of the anode and cathode, from the anode side only, and from the cathode side only. We adapted galvanostatic mode to

keep the reaction rate of the SRM constant. The current was set to 900 μA , which was a suitable current value to generate detectable amounts of products and to evaluate the voltage change by the UV light irradiation. We conducted this experiment under identical conditions to the experiment using the GPEC system described above.

(a)



(b)



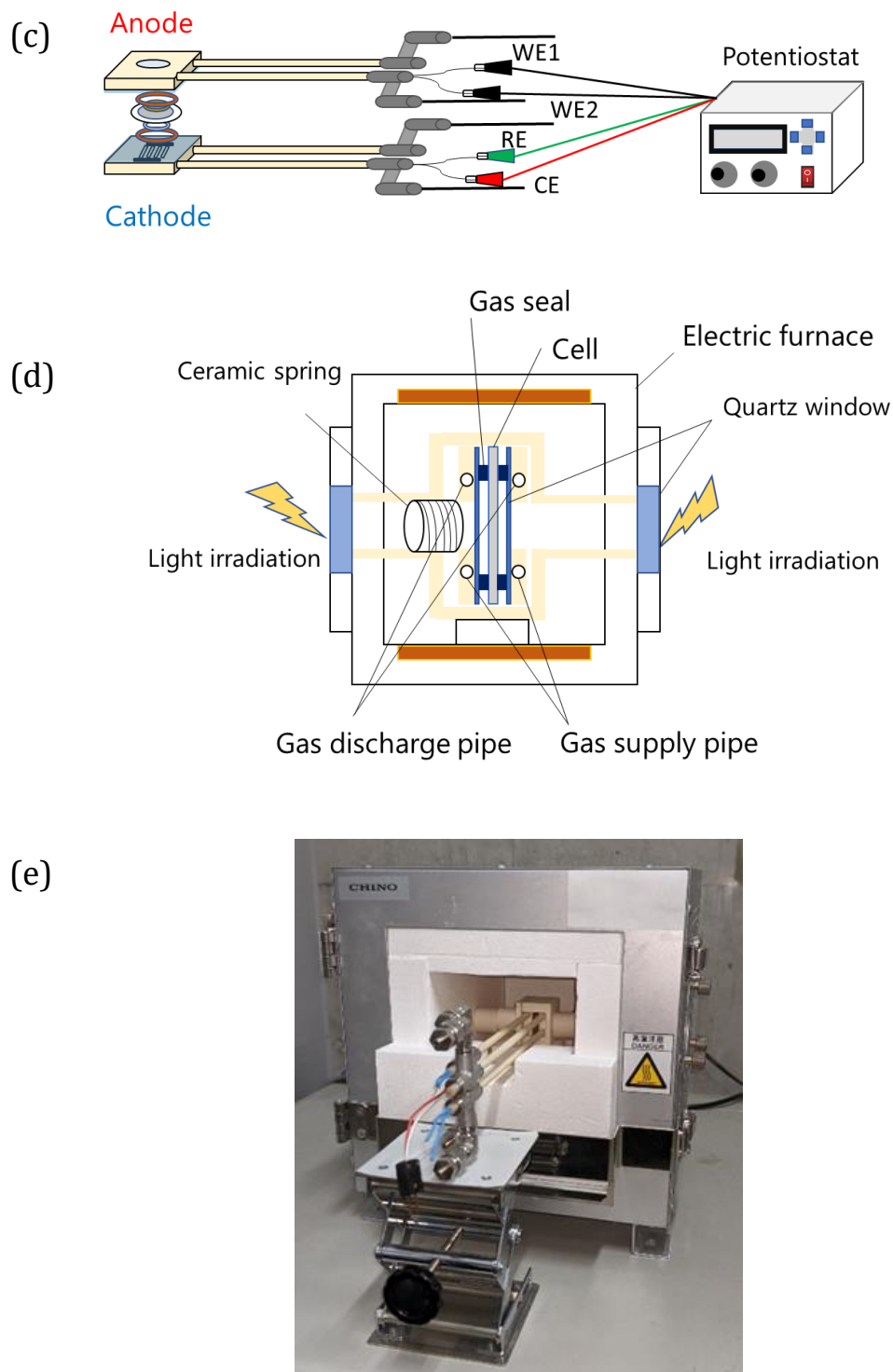


Figure S1. Schematic images and photos of GPEC system. (a) Holder part. (b) Photo of the holder part. (c) Electrical wiring between potentiostat and cell. (d) Holder inserted into an electric furnace. (e) Photo of the holder inserted into the electric furnace.

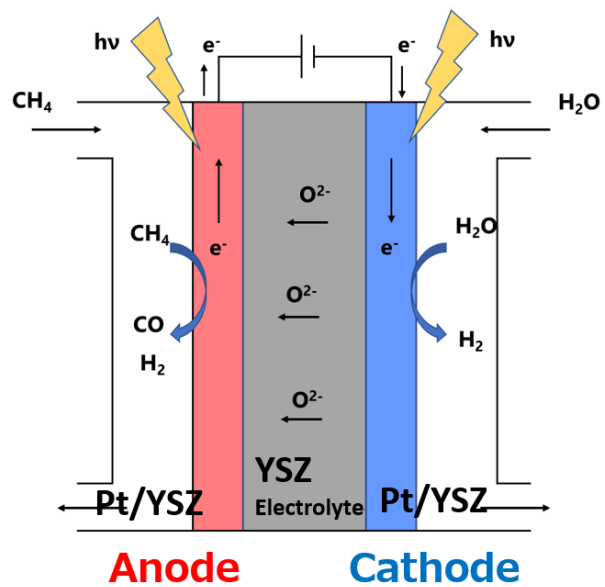
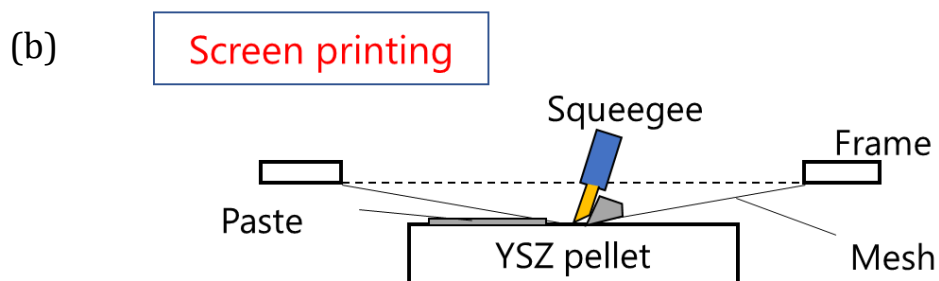
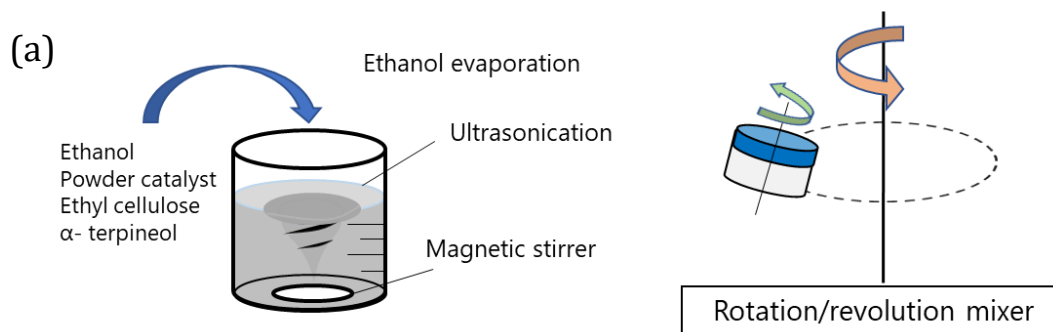


Figure S2. Schematic illustration of SRM using the GPEC system.



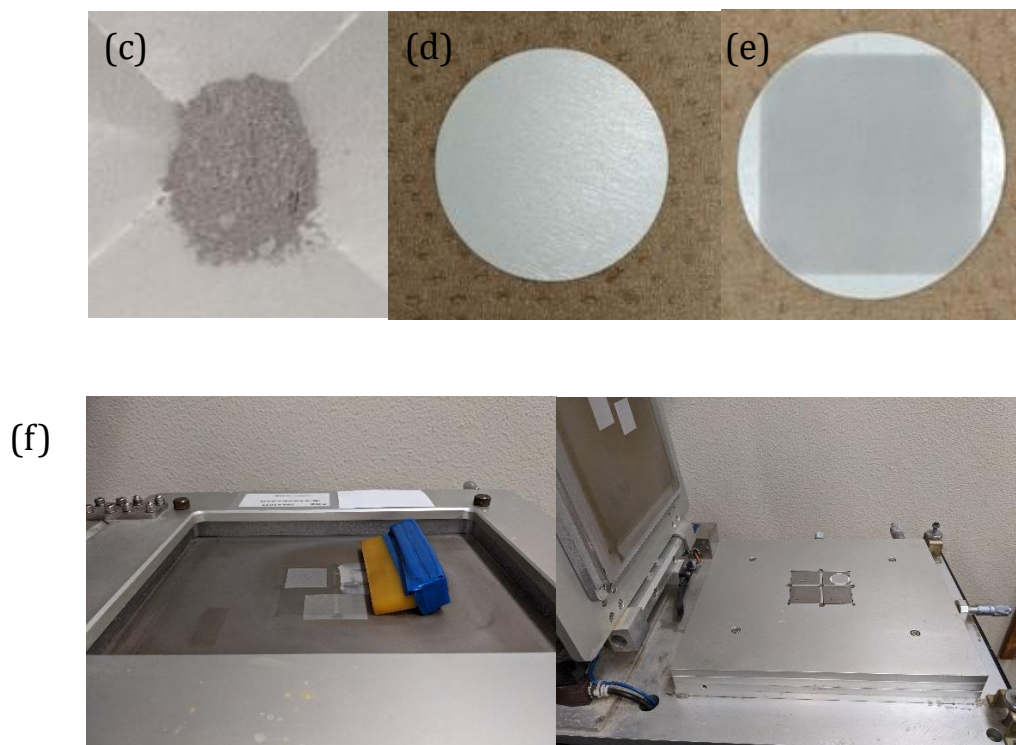


Figure S3. Schematic illustration and photos of cell fabrication. (a) Preparation for the highly dispersed powder catalyst paste. (b) Schematic image of screen printing. (c) Photo of the Pt/YSZ powder catalyst. (d) Photo of the YSZ pellet. (e) Photo of the cell used in the GPEC system. (f) Photos of screen printing.

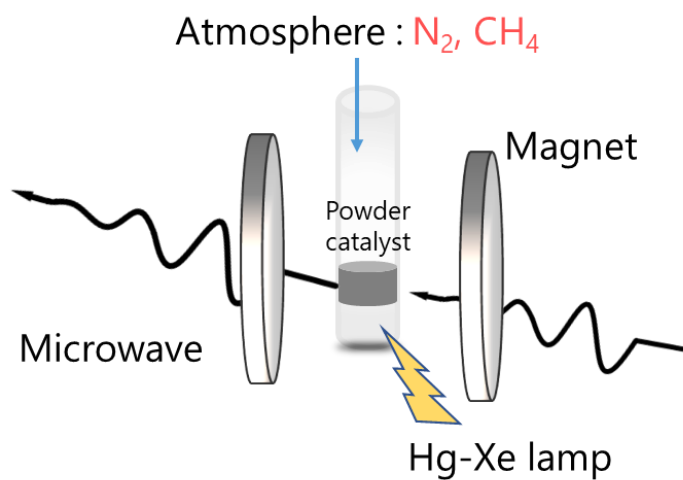


Figure S4. Schematic illustration of ESR measurement.

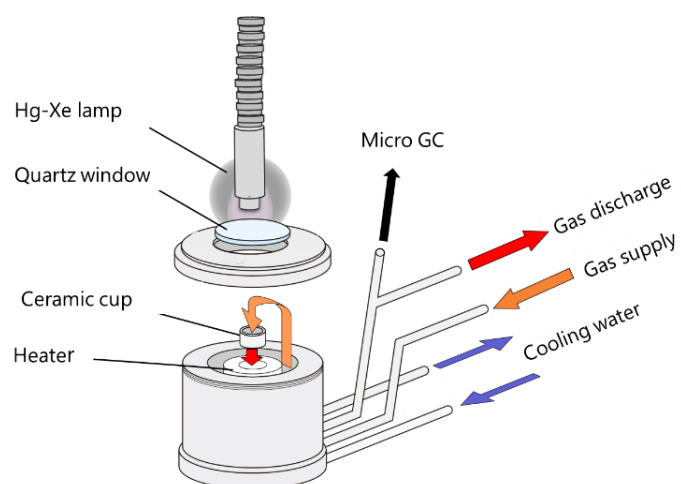


Figure S5. Schematic illustration of the reactor for the SRM test with Pt/YSZ powder catalyst.

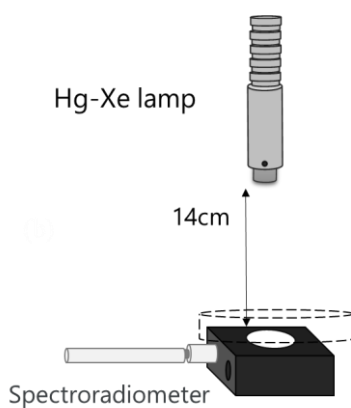


Figure S6. Schematic illustration of measurement of the transmitted light of the cell.

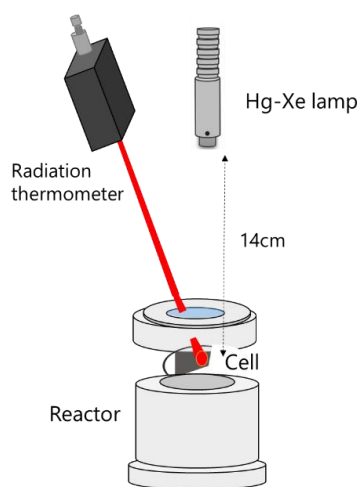


Figure S7. Schematic illustration of measurement of the surface temperature of the cell under UV light irradiation.

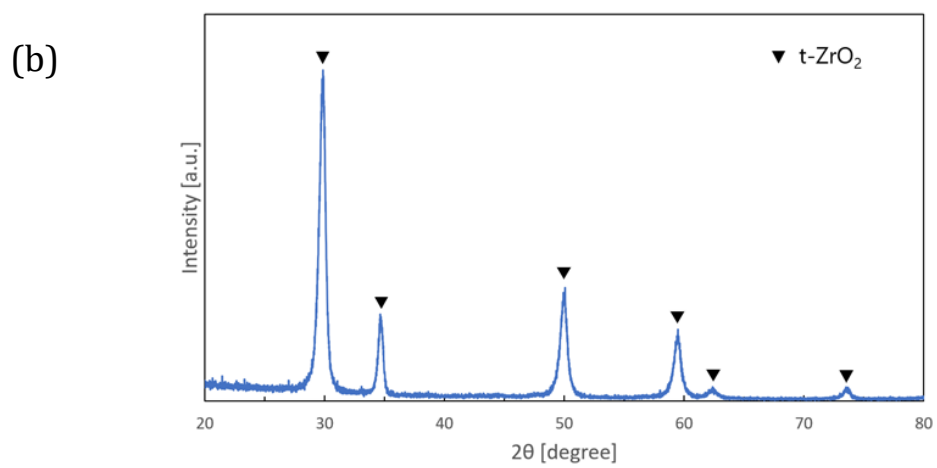
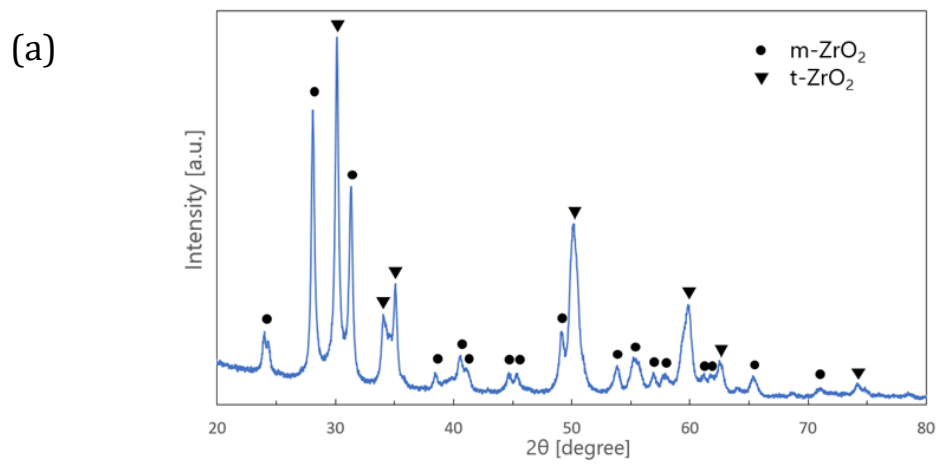
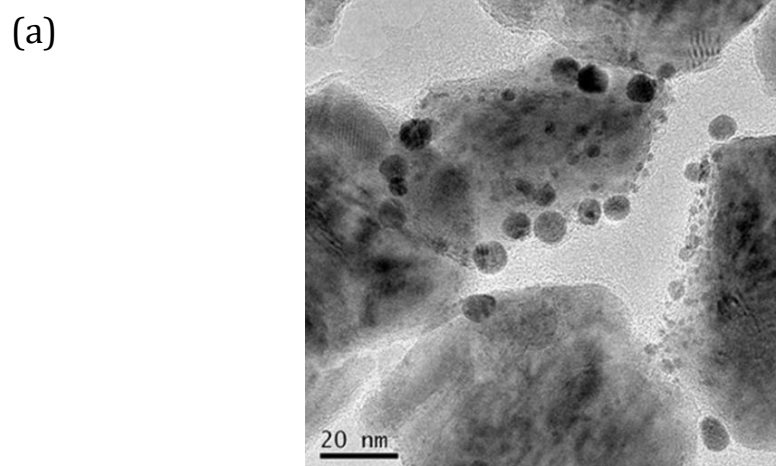
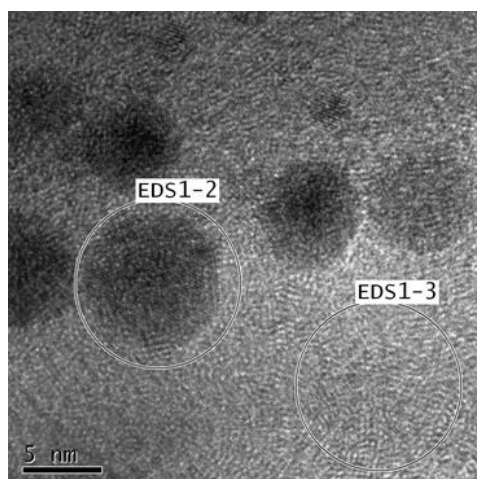


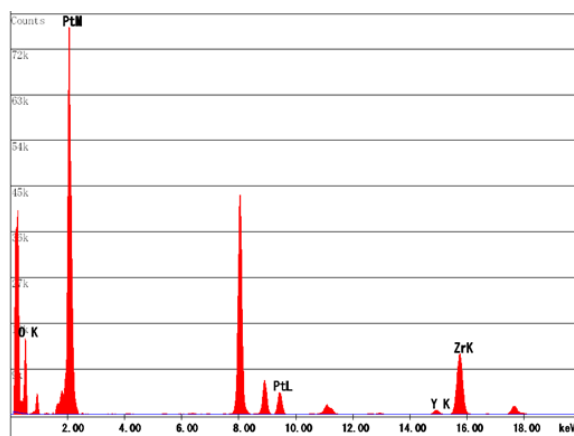
Figure S8. The XRD patterns of (a) the Pt/YSZ powder catalyst and (b) the YSZ pellet before screen printing.



(b)



(c)



(d)

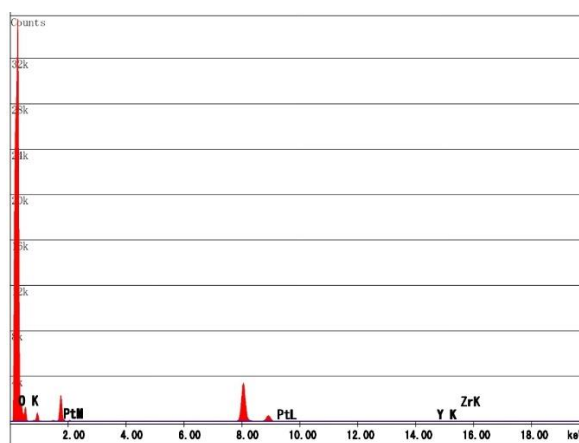


Figure S9. (a) The TEM image of the Pt/YSZ powder catalyst. (b) Analysis range (1-2) and (1-3) of EDS. (c) EDS spectrum (1-2). (d) EDS spectrum (1-3).

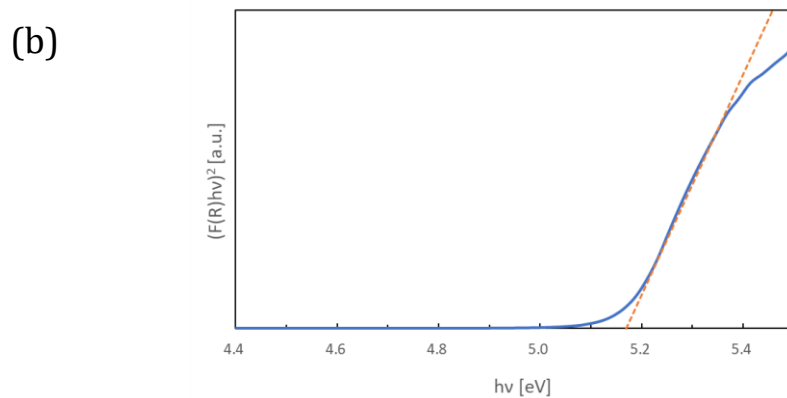
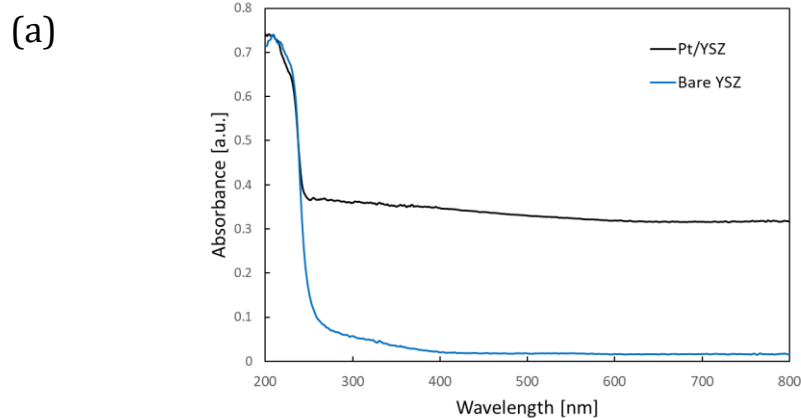


Figure S10. (a) The UV-Vis absorption spectra of the YSZ powder used for the Pt/YSZ powder catalyst and the Pt/YSZ powder catalyst. (b) The Tauc plot of the YSZ powder.

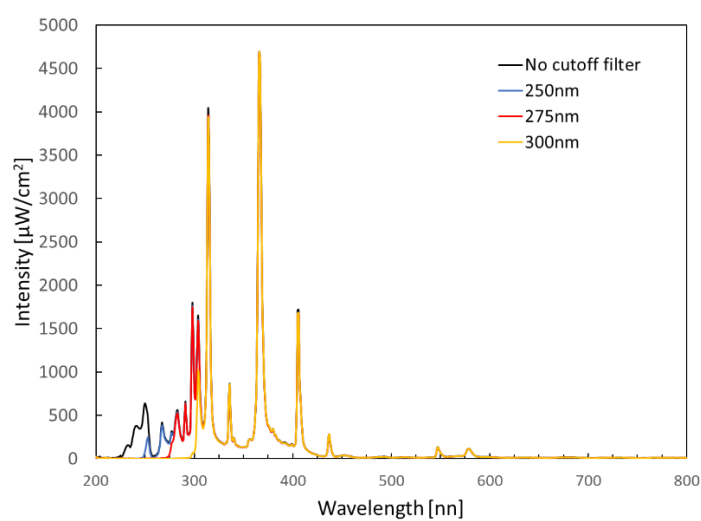


Figure S11. The spectrum of the Hg-Xe lamp with various cutoff filters.

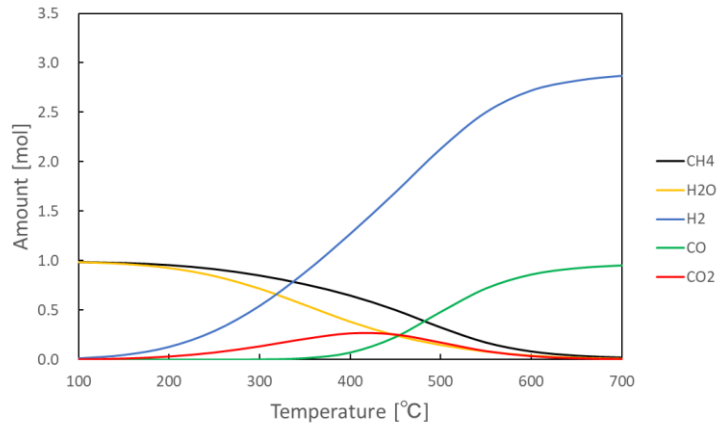


Figure S12. Thermodynamic limits of SRM calculated using NASA-CEA.

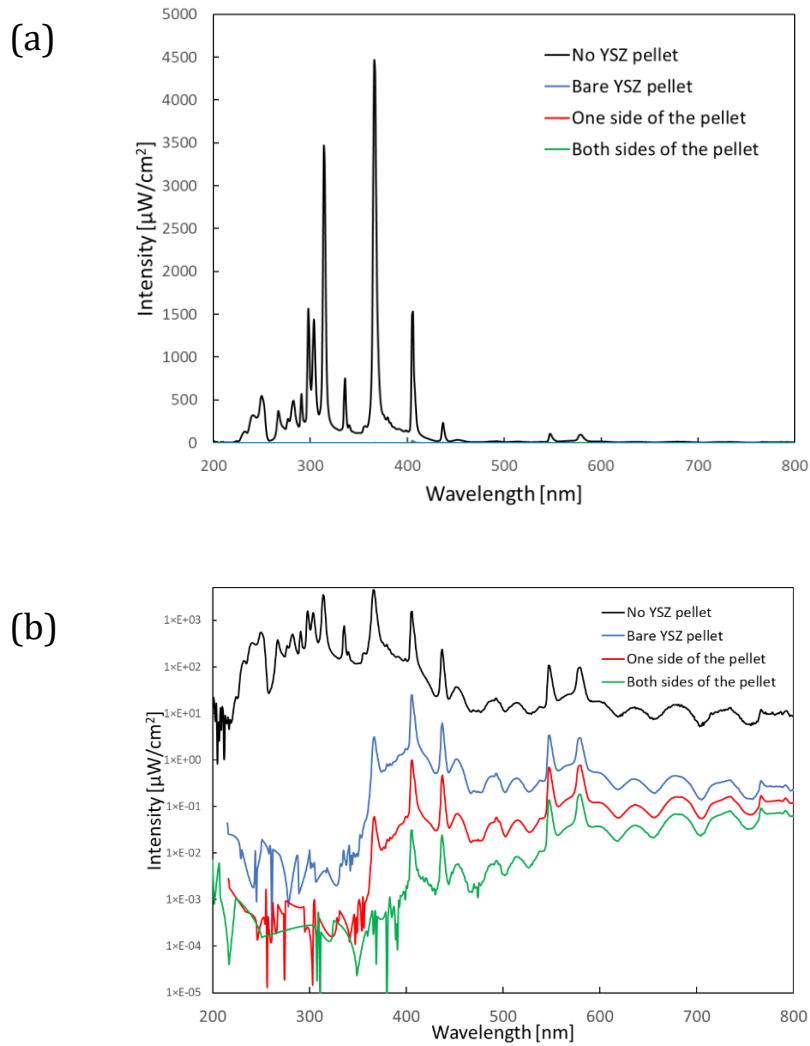


Figure S13. The spectra of the transmitted light of the cell with (a) original and (b) logarithmic scale .

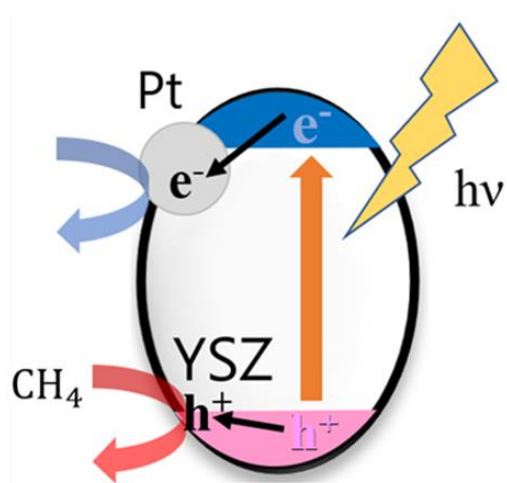


Figure S14. Schematic illustration of the transfer model of photogenerated carriers in the Pt/YSZ powder catalyst under methane atmosphere and UV light irradiation.

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